

PATENT ABSTRACTS OF JAPAN

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(54) ELECTROPHOTOGRAPHIC TONER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a toner excellent in image reproducibility and anti-offsetting property by using a crosslinked resin hardly affected by the breaking of gel at the time of kneading for forming a toner as a binder.

SOLUTION: This toner contains a resin compsn. consisting of a glycidyl group-contg. vinyl resin as a crosslinking agent and a COOH group-contg. vinyl resin as a binder. The glycidyl group-contg. vinyl resin has a wt. average mol.wt. of >10,000 to 100,000 and 0.005-0.1Eq/100g epoxy value. The COOH group-contg. vinyl resin has 1-30mgKOH/g acid value and 40-70° C glass transition temp.

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CLAIMS

[Claim(s)]

[Claim 1] The toner for electrophotography with which the binder concerned makes the glycidyl group content vinyl resin (A) which weight average molecular weight is larger than 10,000, is 100,000 or less, and is epoxy value 0.005-0.1Eq / 100g a cross linking agent, and is characterized by constituting as a subject the resin constituent which consists of the acid number 1 - 30 mgKOH/g, and COOH radical content vinyl resin (B) whose Tg is 40-70 degrees C in the toner for electrophotography which consists of a coloring agent and a binder at least.

[Claim 2] The toner for electrophotography according to claim 1 whose gel molar fraction contained in a total amount although this binder carried out crosslinking reaction and was obtained by carrying out heating fusion of glycidyl group content vinyl resin (A) and the COOH radical content vinyl resin (B) is 0.1 - 40 % of the weight.

[Claim 3] Per 1Eq of COOH radicals in COOH radical content vinyl resin (B), the toner for electrophotography according to claim 1 which is a mixed ratio used as the glycidyl group content vinyl resin (A) which has 0.01-0.5Eq as a glycidyl group.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the toner for electrophotography for developing an electrostatic-charge image in electrophotography, electrostatic recording, electrostatic printing, etc. It can respond to a high-speed machine in more detail, and is related with the toner for electrophotography which is moreover high resolution and was excellent in image quality.

[0002]

[Description of the Prior Art] Generally, after the electrophotography direction for use in a PPC copying machine or a printer forming the static electricity-latent image on an optical photo conductor, developing this latent image using a toner subsequently and imprinting a toner image on established sheets, such as paper, the approach of carrying out heating sticking by pressure with a hot calender roll is performed. Since this approach is established under heating pressurization, it is quick, moreover is very good, therefore it is very good. [of fixing effectiveness] [of thermal efficiency] However, while thermal efficiency is good in this hot calender roll method, in order that a hot calender roll front face and a toner may contact in the state of melting, a toner carries out adhesion transition on a hot calender roll front face, and there is a problem that this re-transfers and soils on the following covering sheet (offset phenomenon).

[0003] On the other hand, the copying machine points to the direction of improvement in the speed, the speed of a fixing roll also becomes quick inevitably, and the toner which can be established with short-time heating is demanded. Although it is thought that what is necessary is it to be required to be a quantity flow at the time of melting, and just to make small molecular weight of the resin used for a toner for that purpose in order to make it established as much as possible for a short time, the cohesive force of the resin by molecular weight fall is insufficient, and it becomes easy to generate an offset phenomenon conversely, and is not desirable. For this reason, although a fluidity usually falls victim to some extent, mixed use is carried out with the thing of low molecular weight, and the thing of the amount of macromolecules, and balance is given for the cohesive force which the thing of the amount of macromolecules has, and the fluidity which the thing of low molecular weight has. As such an example, they are a Japanese Patent Publication No. 55-No. 6895 official report, JP,63-32180,B, and USP 4,921,771. The technique concerning a number etc. is proposed. However, although the copying machine of a 10-30-sheet the copy speed for /was conventionally in use, development Kamiichi also of many 50-100-sheet high-speed copying machines like [for /] is carried out in recent years. To such improvement in the speed, it is not yet enough and there is a case where it corresponds by amelioration of a machine etc., plentifully. That is, the silicone oil was applied in cloth or paper on the surface of the hot calender roll, and offset is prevented. In this case, since a facility of a machine becomes complicated, repair of a machine and management become complicated, lead to a cost rise, and are not desirable. Therefore, development of the toner for fixing (oilless fixing method) which is a toner for high-speed machines, and does not need use of oil, such as a silicone oil, is desired. Moreover, a manuscript becomes very beautiful with the rise of the printer engine performance, and the appearance of the copying machine which can reproduce a manuscript as faithfully as possible has also come to be required strongly. the size completely same as a line a deep line a thick thin line is thick and thin [a line] and thin is thin, and deep [a line] and very thin — it is required for the same form to reproduce a manuscript as faithfully as possible, and, for that, it can reappear also by the very fine line — as — the particle size of a toner — small — it is necessary to carry out — the diameter-sized toner of a granule — **** — last — it is becoming like. However, a thin line becomes thick and is not desirable, if a toner is crushed and it spreads greatly with a hot calender roll at the time of fixing, even if it uses the diameter-sized toner of a granule with much trouble. Moreover, the high-definition toner is desired for the flare of the toner when being fixed to paper to be able to maintain the magnitude of the original toner as much as possible with high resolution.

[0004] Although what is necessary is to crush a toner with a hot calender roll, to make [many / as possible] the amount of macromolecules at the time of fixing in order not to spread greatly and to carry out, and just to give elasticity to a toner, productivity is downed that it is hard to grind in that case, and it becomes a problem. Moreover, although generally moreover diameter[of a granule]-ized to about 7micro at high resolution to make it a high-definition toner, in order to make it easy to grind, if low molecular weight is increased, fines will carry out abundant generating at the time of grinding, productive efficiency falls, and a production cost goes up sharply and poses a problem.

[0005] On the other hand, many toners using crosslinked polymer as the offset prevention approach in development

of the toner for oilless fixing methods are also proposed. For example, the approach using the crosslinked polymer manufactured by the emulsion-polymerization method is indicated by JP,60-36582,B. In this case, it was very difficult for offset-proof nature not to become good although a grindability will become good, if a grindability gets worse and the amount of another side crosslinked polymer decreases, although offset-proof nature will become good, if the crosslinked polymer used contains a part for gel 50 to 99% and a part for this gel is made [many], but to satisfy both offset-proof nature and grindability. Moreover, in order to stabilize an emulsification particle at the time of crosslinked polymer manufacture, it is necessary to make a dispersant and a distributed assistant use together by this approach. Since these dispersants have a bad influence on an electrical property, especially charge stability in order to tend to absorb moisture, they have the need of removing these as much as possible, after crosslinked polymer manufacture. However, an effort great for washing these and removing completely is required, and the displacement of wash water also increases and the processing is also serious. moreover, USP4,966,829 a number official report — a gel component — 0.1 – 60 percentage-by-weight implication and tetrahydrofuran extractives — setting — the molecular weight of the Maine peak — the molecular weight of 1,000–25,000 and a subpeak, or a shoulder — 3,000–150,000 the toner containing the vinyl system polymer which it has at least one is good — the purport indication is carried out. However, the method of manufacturing this was the suspension method, and since the dispersant and the distributed assistant were made to use together like an emulsion-polymerization method also in this case at the time of manufacture, there was the completely same problem as the above-mentioned emulsion polymerization. For this reason, this invention person etc. has developed the resin (USP No. 4,963,456) by the solution polymerization method as fixable good resin for toners.

[0006] Although the resin by the solution polymerization method removes the solvent after polymerization termination, since all low volatile components, such as an unreacted residual monomer and a decomposition product of an initiator, can be distilled off at this time, it is thought with very few impurities that stable homogeneous resin is obtained electrically and the optimal thing for toners is obtained. However, manufacture of the crosslinked polymer by the solution polymerization method had a problem of it becoming impossible for the wye ZEMBERUGU effectiveness (for resin to coil around a stirring rod) to occur and manufacture. Therefore, this invention person etc. is the approach of macromolecule-izing as much as possible with bulk etc. further (USP No. 5,084,368). It developed. However, a limitation is one of the things of the amount of macromolecules which can be manufactured, and it had not resulted till the place which conquers offset nature completely. Moreover, in JP,60-38700,B, it is a glycidyl group content monomer 3 – 40% Copolymer which it has (A) Cross-linking compound (B) The toner of reverse charge was generated by the test of a long period of time [that the toner binder which carried out / the binder / heating mixing and was manufactured is good] although the purport indication is carried out, since an epoxy group is as abundant ** in this toner, and the problem was produced in endurance.

[0007]

[Problem(s) to be Solved by the Invention] By making a bridge construct by the specific ratio using the resin which has COOH manufactured by the solution polymerization method, and the compound which has a glycidyl group, this invention persons could respond to the high-speed machine, and balance of fixable, offset nature, and blocking nature was good, and they developed the technique of obtaining the toner excellent also in a grindability, productive efficiency, an electrical property, and charge stability (JP,06-011890,A and JP,06-222612,A). However, in order that superfluous SHIEA might start a bridge formation component and gel might receive cutting at the time of kneading in a toner production process, hot elasticity became inadequate and the problem that neither aggravation of the image after fixing nor sufficient offset-proof effectiveness was acquired arose. By improving the molecular weight and epoxy value containing a glycidyl group of a cross linking agent, as a result of inquiring wholeheartedly that this invention persons should satisfy these demands Cutting of the gel at the time of kneading of a toner production process is reduced. Image repeatability, The binder for toners which effectiveness appeared in offset-proof nature, and the balance of fixable, offset nature, and blocking nature has been sharply improved, and was excellent also in a grindability, productive efficiency, an electrical property, and charge stability was found out, and this invention was completed.

[0008] That is, this invention is 1. In the toner for electrophotography which consists of a coloring agent and a binder at least Weight average molecular weight is larger than 10,000, and the binder concerned is 100,000 or less. The glycidyl group content vinyl resin (A) which is epoxy value 0.005–0.1Eq / 100g is made into a cross linking agent. The acid number 1 – 30 mgKOH/g, the toner for electrophotography characterized by constituting as a subject the resin constituent which consists of COOH radical content vinyl resin (B) whose Tg is 40–70 degrees C, 2) The toner for electrophotography according to claim 1 whose gel molar fraction contained in a total amount although this binder carried out crosslinking reaction and was obtained by carrying out heating fusion of glycidyl group content vinyl resin (A) and the COOH radical content vinyl resin (B) is 0.1 – 40 % of the weight, 3) It is the toner for electrophotography according to claim 1 which is a mixed ratio per 1Eq of COOH radicals in COOH radical content vinyl resin (B), and used as the glycidyl group content vinyl resin (A) which has 0.01–0.5Eq as a glycidyl group.

[0009]

[Means for Solving the Problem] By improving the molecular weight and epoxy value containing a glycidyl group of a cross linking agent, as a result of inquiring wholeheartedly that this invention persons should satisfy these demands Cutting of the gel at the time of kneading of a toner production process is reduced. Image repeatability, The binder for toners which effectiveness appeared in offset-proof nature, and the balance of fixable, offset nature, and blocking nature has been sharply improved, and was excellent also in a grindability, productive efficiency, an

electrical property, and charge stability was found out, and this invention was completed.

[0010] That is, this invention is 1. In the toner for electrophotography which consists of a coloring agent and a binder at least Weight average molecular weight is larger than 10,000, and the binder concerned is 100,000 or less. The glycidyl group content vinyl resin (A) which is epoxy value 0.005-0.1Eq / 100g is made into a cross linking agent. The acid number 1 - 30 mgKOH/g, the toner for electrophotography characterized by constituting as a subject the resin constituent which consists of COOH radical content vinyl resin (B) whose Tg is 40-70 degrees C, 2) The toner for electrophotography according to claim 1 whose gel molar fraction contained in a total amount, although this binder carries out crosslinking reaction and might be built by carrying out heating fusion of glycidyl group content vinyl resin (A) and the COOH radical content vinyl resin (B) is 0.1 - 40 % of the weight, 3) It is the toner for electrophotography according to claim 1 which is a mixed ratio per 1Eq of COOH radicals in COOH radical content vinyl resin (B), and used as the glycidyl group content vinyl resin which has 0.01-0.5Eq as a glycidyl group. [0011]

[Embodiment of the Invention] The thing whose weight average molecular weight is 12,000-30,000 preferably 100,000 or less as glycidyl group content vinyl resin (A) in this invention more greatly than 10,000 and whose epoxy value is 0.005-0.1Eq / 100g is desirable. Glycidyl group content vinyl resin is resin which copolymerized the vinyl monomer containing a glycidyl group, and other vinyl monomers, and was obtained. Even if weight average molecular weight compounds a bridge formation object or less by 10,000, cutting of the gel in kneading of a toner production process is intense, and a problem arises to the image repeatability after fixing, and offset-proof nature. Conversely, 100,000 If high, fixable will get worse. Moreover, the thing of epoxy value of 0.005-0.1Eq / the range of 100g is desirable. 0. If it is in 0.05Eq / 100g or less, the amount of gel generation cannot perform amelioration of offset nature few. 0.1 Eq / 100g Above, even if it compounds a bridge formation object, cutting of the gel in a toner production process is intense, and a problem arises to image repeatability and offset-proof nature.

[0012] It is 0.1 - 40% in the resin to which crosslinking reaction of glycidyl group content vinyl resin (A) and the COOH radical content vinyl resin (B) is carried out by carrying out heating fusion in this invention. It is desirable to contain the gel molar fraction. It is 5 - 20% still more preferably. 0.1% of gel molar fractions Bridge formation object sufficient in below does not generate, and the effectiveness of offset-proof nature is not discovered. Moreover, at 40% or more, a lifting fluidity gets worse [most] gelation and a problem appears also in fixable. Moreover, it is a glycidyl group per 1Eq of COOH radicals in COOH radical content vinyl resin (B). The mixed ratio used as the glycidyl group content vinyl resin (A) which has 0.01-0.5Eq is desirable. It is 0.03-0.2Eq still more preferably.

[0013] The glycidyl group content vinyl monomer used for manufacture of the glycidyl group content vinyl resin (A) used in this invention has metaglycidyl acrylate, acrylic-acid beta methyl glycidyl, metaglycidyl acrylate, desirable methacrylic acid beta methyl glycidyl, etc.

[0014] Moreover, as a COOH radical content vinyl monomer used for manufacture of the COOH radical content vinyl resin (B) used in this invention, it is monoester of partial saturation dibasic acids, such as an acrylic acid, a methacrylic acid, a maleic anhydride, a maleic acid, boletic acid, a cinnamon acid, boletic acid methyl, boletic acid ethyl, boletic acid propyl, boletic acid butyl, boletic acid octyl, maleic-acid methyl, maleic-acid ethyl, maleic-acid propyl, maleic-acid butyl, and maleic-acid octyl.

[0015] As a glycidyl group content vinyl monomer and a COOH radical content vinyl monomer, and a vinyl monomer to copolymerize For example, styrene, such as styrene, P-methyl styrene, alpha methyl styrene, and vinyltoluene A methyl acrylate, an ethyl acrylate, acrylic-acid propyl, butyl acrylate, Acrylic-acid octyl, acrylic-acid cyclohexyl, acrylic-acid stearyl, Acrylic-acid benzyl, acrylic-acid furfuryl, acrylic-acid hydroxyethyl, Acrylic ester, such as acrylic-acid hydroxy butyl, acrylic-acid dimethyl aminomethyl, and acrylic-acid dimethylaminoethyl Methacrylic acid methyl, methacrylic acid ethyl, methacrylic acid propyl, Methacrylic acid butyl, methacrylic acid octyl, methacrylic acid cyclohexyl, Methacrylic acid stearyl, methacrylic acid benzyl, methacrylic acid furfuryl, Methacrylic acid hydroxyethyl, methacrylic acid hydroxy butyl, Methacrylic acid ester, such as methacrylic acid dimethyl aminomethyl and methacrylic acid dimethylaminoethyl Boletic acid dimethyl, boletic acid dibutyl, boletic acid dioctyl, The diester of partial saturation dibasic acids, such as maleic-acid dimethyl, dibutyl maleate, and dioctyl maleate There are acrylonitrile, meta-acrylonitrile, acrylamide, meta-acrylamide, N permutation acrylamide, N permutation meta-acrylamide, an amide of a kind, etc., and at least one sort of these vinyl monomers is used. As a vinyl monomer especially desirable in these, they are styrene, acrylic ester, methacrylic acid ester, boletic acid dialkyl ester, acrylonitrile, acrylamide, methacrylamide, etc.

[0016] COOH radical content vinyl resin (B) has the acid number 1 - 30 KOHmg/g, and desirable resin whose Tg is 40-70 degrees C. The acid number 5 - 20 KOHmg/g, and Tg are 50-60 degrees C still more preferably. If Tg causes blocking below 40 degrees C and Tg becomes 70 degrees C or more preferably, softening temperature will go up, fixable gets worse, and the toner of this purpose is not obtained. The COOH content in COOH radical content vinyl resin (B) has desirable 1 - 30 KOHmg/g as the acid number. Or less by one, since the reacting weight per monad decreases, image repeatability and offset nature run short that it is hard to become the amount of macromolecules. Moreover, 30 KOHmg/g Above, cutting of the gel in kneading of a toner production process is intense, and image repeatability and offset nature get worse.

[0017] The number average molecular weight and the weight average molecular weight in this invention are that for which it asked by the GPC method, and are the conversion molecular weight which created the calibration curve with mono dispersion standard polystyrene. A Measuring condition is as follows.

GPC equipment TETRAHYDROFURAN style **; JASCO TWINCLE HPLCDETECTOR ; SHODEX RI SE-31COLUMN ; SHODEX GPCA-80M*2+KF-802 ** Intermediation ; The gel molar fraction in; 1.2ml/min. this invention computes

the ethyl-acetate insoluble matter to the resin whole quantity when dissolving the resin 5 section in the ethyl-acetate 95 section enough.

[0018]

[Example] Next, an example explains this invention concretely. In addition, henceforth, especially the "section" expresses the weight section, unless it refuses.

[The example of manufacture of glycidyl group content vinyl resin (A)]

The styrene 65 section which taught and carried out the temperature up of the example of manufacture A-1 xylene 75 section to the flask which carried out the nitrogen purge, and carried out the mixed dissolution beforehand under xylene reflux, the acrylic-acid n-butyl 30 section, the metaglycidyl acrylate 5 section, G t - Continuation addition of the butyl peroxide 1 section is carried out over 5 hours, and reflux is continued for further 1 hour. After that internal temperature It kept at 130 degrees C, and by performing the ** monomer polymerization of 2 hours twice, the reaction was completed and polymerization liquid was obtained. The flash plate of this was carried out into the besel of 10mmHg 160 degrees C, and the solvent etc. was distilled off. The weight average molecular weight of the obtained vinyl resin was 40,000, epoxy value 0.035Eq / 100g.

[0019] It sets for the example A-1 of example of manufacture A-2 manufacture, and is G t. - They are the four sections and metaglycidyl acrylate about the butyl peroxide 1 section. Vinyl resin was obtained completely like the example A-1 of manufacture except having made the 13 sections and the styrene 65 section into the 57 sections for the five sections. Although obtained, the physical-properties value was shown in Table -1.

It sets for the example A-2 of example of manufacture A-3 manufacture, and is G t. - Vinyl resin was obtained completely like the example A-2 of manufacture except having made the butyl peroxide 4 section into the eight sections. Although obtained, the physical-properties value was shown in Table -1.

[0020] Vinyl resin was obtained completely like the example A-2 of manufacture except having made the 16 sections and the styrene 57 section into the 54 sections for the metaglycidyl acrylate 13 section in the example A-2 of example of manufacture A-4 manufacture. Although obtained, the physical-properties value was shown in Table -1.

It sets for the example A-1 of example of manufacture A-5 manufacture, and is G t. - Vinyl resin was obtained completely like the example A-1 of manufacture except having made [the butyl peroxide 1 section] the one section and the styrene 65 section into the 69 sections for the four sections and the metaglycidyl acrylate 5 section. Although obtained, the physical-properties value was shown in Table -1.

[0021] It sets for the example A-5 of example of manufacture A-6 manufacture, and is G t. - Vinyl resin was obtained completely like the example A-5 of manufacture except having made the butyl peroxide 4 section into the eight sections. Although obtained, the physical-properties value was shown in Table -1.

It sets for the example A-5 of example of manufacture A-7 manufacture, and is the metaglycidyl acrylate 1 section. Vinyl resin was obtained completely like the example A-5 of manufacture except having made the 0.5 sections and the styrene 69 section into the 69.5 sections. Although obtained, the physical-properties value was shown in Table -1.

[0022] It sets for the example A-1 of example of manufacture A-8 manufacture, and is G t. - Vinyl resin was obtained completely like the example A-1 of manufacture except having made [the butyl peroxide 1 section] the one section and the styrene 65 section into the 69 sections for the 0.4 sections and the metaglycidyl acrylate 5 section. Although obtained, the physical-properties value was shown in Table -1.

It sets for the example A-8 of example of manufacture A-9 manufacture, and is G t. - Vinyl resin was obtained completely like the example A-8 of manufacture, except having made the butyl peroxide 0.4 section into the 0.1 sections. Although obtained, the physical-properties value was shown in Table -1.

[0023] Vinyl resin was obtained completely like the example A-8 of manufacture except having made the 0.5 sections and the styrene 69 section into the 69.5 sections for the metaglycidyl acrylate 1 section in the example A-8 of example of manufacture A-10 manufacture. Although obtained, the physical-properties value was shown in Table -1.

It sets for the example A-1 of example of manufacture A-11 manufacture, and is G t. - Vinyl resin was obtained completely like the example A-1 of manufacture except having made [the butyl peroxide 1 section] the 13 sections and the styrene 65 section into the 57 sections for the 0.4 sections and the metaglycidyl acrylate 5 section. Although obtained, the physical-properties value was shown in Table -1.

[0024] It sets for the example A-11 of example of manufacture A-12 manufacture, and is G t. - Vinyl resin was obtained completely like the example A-11 of manufacture except having made the butyl peroxide 0.4 section into the 0.1 sections. Although obtained, the physical-properties value was shown in Table -1.

Vinyl resin was obtained completely like the example A-11 of manufacture except having made the 16 sections and the styrene 57 section into the 54 sections for the metaglycidyl acrylate 13 section in the example A-11 of example of manufacture A-13 manufacture. Although obtained, the physical-properties value was shown in Table -1.

[0025] [The example of manufacture of COOH radical content vinyl resin (B)]

The example of manufacture B-1 styrene 57.4 section, the acrylic-acid n-butyl 11.9 section, and methacrylic acid 0.7 It is styrene 100 to the solution which consists of the section and the xylene solvent 30 section. Per [0.6] section G t of the section - About what dissolved butyl peroxide in homogeneity, it is internal temperature 190 ** internal pressure. 5l. held to 6kg/cm2 By 750 cc/hr, the reactor was supplied continuously, the polymerization was carried out to it, and low-molecular-weight polymerization liquid was obtained.

[0026] It taught independently the flask which carried out the nitrogen purge of the styrene 75 section, the acrylic-

acid n-butyl 23.5 section, and the methacrylic acid 1.5 section as a vinyl monomer, and maintained at the internal temperature of 120 degrees C at the after [a temperature up] said temperature, and bulk polymerization was performed for 10 hours. The conversion at this time was 51%. Subsequently, 0.1 section xylene of the dibutyl peroxide which added the xylene 50 section and carried out the mixed dissolution beforehand Over 8 hours, continuation addition was carried out, the ** monomer polymerization was carried out for further 2 hours, keeping the 50 sections at 130 degrees C, the polymerization was completed, and the amount polymerization liquid of macromolecules was obtained. Subsequently, after mixing the low-molecular-weight polymerization liquid 100 above-mentioned section and the amount polymerization liquid of giant molecules 60 section, the flash plate of this was carried out into the bessel of 160 **10mmHg, and the solvent etc. was distilled off. Tg of the obtained vinyl resin was 59 degrees C, and the acid number was 7.3.

[0027] When manufacturing low-molecular-weight polymerization liquid in the example B-1 of example of manufacture B-2 manufacture, vinyl resin was completely obtained like the example B-1 of manufacture except having made the 54.6 sections and the methacrylic acid 0.7 section into the 3.5 sections for the styrene 57.4 section. Although obtained, the physical-properties value was shown in Table -2.

When manufacturing low-molecular-weight polymerization liquid in the example B-1 of example of manufacture B-3 manufacture, vinyl resin was completely obtained like the example B-2 of manufacture except having made the 53.2 sections and the methacrylic acid 0.7 section into the 4.9 sections for the styrene 57.4 section. Although obtained, the physical-properties value was shown in Table -1.

[0028] When making the 58.1 sections and the methacrylic acid 0.7 section into the 0.0 sections for the styrene 57.4 section when manufacturing low-molecular-weight polymerization liquid in the example B-1 of example of manufacture B-4 manufacture, and manufacturing the amount polymerization liquid of giant molecules, vinyl resin was completely obtained like the example B-2 of manufacture except having made the 76.0 sections and the methacrylic acid 1.5 section into the 0.5 sections for the styrene 75 section. Although obtained, the physical-properties value was shown in Table -1.

When manufacturing the amount polymerization liquid of giant molecules in the example B-4 of example of manufacture B-5 manufacture, vinyl resin was completely obtained like the example B-4 of manufacture except having made the 76.3 sections and the methacrylic acid 1.5 section into the 0.2 sections for the styrene 75 section. Although obtained, the physical-properties value was shown in Table -2.

[0029] When manufacturing low-molecular-weight polymerization liquid in the example B-1 of example of manufacture B-6 manufacture, vinyl resin was completely obtained like the example B-1 of manufacture except having made the 50.4 sections and the acrylic-acid n-butyl 11.9 section into the 18.9 sections for the styrene 57.4 section. Although obtained, the physical-properties value was shown in Table -2.

When manufacturing low-molecular-weight polymerization liquid in the example B-1 of example of manufacture B-7 manufacture, vinyl resin was completely obtained like the example B-1 of manufacture except having made the 46.9 sections and the acrylic-acid n-butyl 11.9 section into the 22.4 sections for the styrene 57.4 section. Although obtained, the physical-properties value was shown in Table -2.

[0030] In case low-molecular-weight polymerization liquid is manufactured in the example B-1 of example of manufacture B-8 manufacture, they are the 61.6 sections and the acrylic-acid n-butyl 11.9 section about the styrene 57.4 section. Vinyl resin was completely obtained like the example B-1 of manufacture except having considered as the 7.7 sections. Although obtained, the physical-properties value was shown in Table -2.

In case low-molecular-weight polymerization liquid is manufactured in the example B-1 of example of manufacture B-9 manufacture, they are the 65.1 sections and the acrylic-acid n-butyl 11.9 section about the styrene 57.4 section. Vinyl resin was completely obtained like the example B-1 of manufacture except having considered as the 4.2 sections. Although obtained, the physical-properties value was shown in Table -2.

[0031] It carried out after mixing with the Henschel mixer, and the kneading reaction of the vinyl resin 3 section obtained in the example A-1 of example 1 manufacture and the vinyl resin 97 section obtained in the example B-1 of manufacture was carried out by 200 ** with the biaxial kneading machine (KEXN S-40 mold, Kurimoto make). After cooling / grinding, the carbon black MA100(Mitsubishi Kasei make) 8 section, and polypropylene wax (bis-call 550 P) Eye ZENSU pyrone black TRH1 section addition is carried out as the five sections and an electric charge regulator, and they are after mixing and a biaxial kneading machine (PCM-30 mold, IKEGAI iron steel) with a Henschel mixer again. It was made to knead at 150 degrees C. Subsequently, it cools, grinds and classifies and is abbreviation. The 7-micron toner was obtained. This toner 3 The section and the carrier 97 section are mixed, it considers as a developer, a commercial high-speed copying machine is converted, and the result which was made to write an image and was evaluated is shown in Table -3.

[0032] In examples 2, 3, and 4 and five examples 1, it considered as examples 2, 3, 4, and 5 respectively completely like the example 1 except having used the vinyl resin obtained in the example A-1 of manufacture as the example A-2 of manufacture, and the vinyl resin obtained by 5, 8, and 11. Those results are shown in Table -3.

[0033] In examples 6, 7, and 8 and nine examples 1, it considered as examples 6, 7, 8, and 9 respectively completely like the example 1 except having made the example B-2 of manufacture, and 4, 6 and 8 the vinyl resin obtained in the example B-1 of manufacture. Those results are shown in Table -3.

[0034] In example 10 example 6, it was made to be completely the same as that of an example 1 except having set to 94/6 the mixed ratio of the vinyl resin obtained in the example A-1 of manufacture, and the vinyl resin obtained in the example B-1 of manufacture from 97/3. The result is shown in Table -3.

[0035] In the examples 1, 2, 3, 4, 5, 6, and 7 of a comparison, and eight examples 1, it considered as the examples 1,

2, 3, 4, 5, 6, 7, and 8 of a comparison respectively completely like the example 1 except having used the vinyl resin obtained in the example A-1 of manufacture as the example A-3 of manufacture, and the vinyl resin obtained by 4, 6, 7, 9, 10, 12, and 13. Those results are shown in Table -4.

[0036] In the examples 9, 10, and 11 of a comparison, and 12 examples 1, it considered as the examples 9, 10, 11, and 12 of a comparison respectively completely like the example 1 except having made the example B-3 of manufacture, and 5, 7 and 9 the vinyl resin obtained in the example B-1 of manufacture. Those results are shown in Table -4.

[0037] In example of comparison 13 example 6, it was made to be completely the same as that of an example 1 except having set to 92/8 the mixed ratio of the vinyl resin obtained in the example A-1 of manufacture, and the vinyl resin obtained in the example B-1 of manufacture from 97/3. The result is shown in Table -4.

[0038] It is from 97/3 about the mixed ratio of the vinyl resin obtained in the example A-1 of manufacture in example of comparison 14 example 1, and the vinyl resin obtained in the example B-1 of manufacture. It was made to be completely the same as that of an example 1 except having made it 100/0. The result is shown in Table -4.

[0039] [The evaluation approach of a toner]

1) The high-speed copying machine (72-sheet copy speed for /) of image repeatability marketing performed the line with a line breadth of about 100 micrometers in the paper to the imprint, it observed with the microscope, and five line breadth was measured. Furthermore, through and five line breadth after making it established were measured for this paper to the fixing machine. It asked for the average of the line breadth before and behind fixing, respectively, and the difference of the line breadth before fixing and the line breadth after fixing estimated as follows.

It is line breadth-fixing front width-of-face $O; \Delta < 5 \mu\text{m} \leq \Delta < 10 \mu\text{m} \rightarrow \Delta = 10 \mu\text{m}$
[0040] after line breadth increment $\Delta = \text{fixing}$. 2) It copied with the high-speed copying machine (72-sheet copy speed for /) of fixable marketing, between this part for solid Kurobe and white ground that were copied was made to go 10 times by the fixed force with a rubber (plastics rubber "MONO" by the dragonfly pencil company), the blackness for solid Kurobe was measured with the ink concentration meter, the residual ratio of a toner was expressed with the ratio of concentration, and 80% or more was made good.

3) The temperature at the time of carrying out an offset nature copy which carries out offset generating was displayed as it was, and 200 degrees C or more were made good.

[0041] 4) Extent of condensation of fine particles after leaving a blocking nature toner for one week under the environment of 50% of temperature relative humidity of 50 degrees C was measured as follows visually.

O; — O; which is not condensed at all — x; with the aggregate which does not get loose even if it often shakes **;
container which will get loose if a container is shaken lightly although condensed slightly — [0042] nodule-ized completely 5) At the time of grindability toner manufacture, a part of thing which carried out biaxial kneading cooling was extracted and ground, step was kept with the grain size of the 16 mesh-on of ten-mesh undershirts, and the jet mill ground. Particle size distribution are searched for for the rate of measurement and grain size (5-20micro) with a Coulter counter.

O Less than [more than; 85%O; 70-85%**; 50-70%x; 50%] [0043]

[Table 1]

製造例A

	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10	A-11	A-12	A-13
M _w	30000	11000	7000	11000	11000	7000	11000	70000	1E+05	70000	70000	1E+05	70000
残率(%)	0.035	0.009	0.009	0.11	0.007	0.007	0.004	0.007	0.007	0.004	0.09	0.09	0.11

[0044]

[Table 2]

製造例B

	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
粘度(mPa·s/g)	7.3	24.5	33.2	0.9	0.4	7.3	7.3	7.3	7.3
T _g (°C)	58	60	61	56	56	44	37	64	72

[0045]

[Table 3]

実施例

	実-1	実-2	実-3	実-4	実-5	実-6	実-7	実-8	実-9	実-10
樹脂A	A-1	A-2	A-5	A-8	A-11	A-1	A-1	A-1	A-1	A-1
樹脂B	B-1	B-1	B-1	B-1	B-1	B-2	B-4	B-6	B-8	B-1
重量比率(B/A)	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	94/6
ゲル分(%)	15	19	7	12	30	8	4	16	14	38
T _g (°C)	59	60	58	59	60	61	56	45	65	60
画像再現性δ(μm)	◎ 3	○ 7	○ 7	○ 6	○ 8	○ 8	○ 9	○ 5	○ 5	◎ 2
定着性(%)	◎ 92	○ 86	◎ 93	◎ 92	△ 82	◎ 90	◎ 94	◎ 97	○ 86	△ 81
オフセット性(°C)	◎ 230	△ 205	△ 210	○ 225	△ 210	△ 210	△ 205	○ 225	◎ 230	◎ 240
保存性	○	○	○	○	○	◎	○	△	◎	○
粉碎性(%)	◎ 90	◎ 89	◎ 90	◎ 90	◎ 88	◎ 90	◎ 91	◎ 89	◎ 90	◎ 88

[0046]

[Table 4]

比較例

	比-1	比-2	比-3	比-4	比-5	比-6	比-7	比-8	比-9	比-10	比-11	比-12	比-13	比-14
樹脂A	A-3	A-4	A-6	A-7	A-9	A-10	A-12	A-13	A-1	A-1	A-1	A-1	A-1	A-1
樹脂B	B-1	B-1	B-1	B-1	B-1	B-1	B-1	B-1	B-3	B-5	B-7	B-9	B-1	B-1
重量比率(B/A)	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	92/8	100/0
ゲル分(%)	11	28	5	4	30	3	36	38	2	1	15	14	45	0
T _g (°C)	59	60	58	58	59	58	61	61	58	58	38	72	62	58
画像再現性δ(μm)	○ 9	○ 9	○ 9	× 11	◎ 2	× 10	○ 8	× 10	× 11	× 13	○	◎	◎	×
定着性(%)	◎ 91	△ 82	◎ 93	◎ 94	× 79	○ 89	× 78	× 79	◎ 93	◎ 94	◎ 98	× 76	× 75	◎ 94
オフセット性(°C)	× 195	× 190	× 195	× 195	◎ 240	× 195	△ 210	△ 200	× 195	× 185	○ 220	◎ 235	◎ 240	× 180
保存性	○	○	○	○	○	○	◎	◎	○	○	×	○	○	○
粉碎性(%)	◎ 90	◎ 88	◎ 91	◎ 90	◎ 88	◎ 90	◎ 87	◎ 88	◎ 90	◎ 91	◎ 90	◎ 90	◎ 87	◎ 90

[0047]

[Effect of the Invention] As shown in Table -3, the toner manufactured by the approach of this invention is excellent in image repeatability and offset-proof nature, and the balance of fixing blocking nature is also good, its grindability is also good and it has the practically excellent engine performance.

[Translation done.]

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(54) 【発明の名称】 電子写真用トナー

(57) 【要約】

【解決手段】 トナー化混練時のゲルの切断の影響の少ない架橋樹脂を結着剤としていることにより、画像再現性、耐オフセット性に優れたトナーを提供する。

【構成】 グリシジル基含有ビニル樹脂を架橋剤とし、C O O H基含有ビニル樹脂より構成される樹脂組成物を結着剤とするトナーである。グリシジル基含有ビニルの重量平均分子量が10,000より大きく100,000以下であり、エポキシ価0.005~0.1Eq/100gである。またC O O H基含有ビニル樹脂の酸価が1~30mgKOH/g、T g が40~70℃である。

【特許請求の範囲】

【請求項1】 少なくとも着色剤と結着剤からなる電子写真用トナーに於いて、当該結着剤が重量平均分子量が10,000より大きく100,000以下であり、エポキシ価0.005～0.1Eq/100gであるグリシジル基含有ビニル樹脂（A）を架橋剤とし、酸価1～30mgKOH/g、Tgが40～70℃であるCOOH基含有ビニル樹脂（B）よりなる樹脂組成物を主体として構成されていることを特徴とする電子写真用トナー。

【請求項2】 該結着剤が、グリシジル基含有ビニル樹脂（A）とCOOH基含有ビニル樹脂（B）とを加熱溶解することにより架橋反応せしめて得られたものの総量中に含まれるゲル分率が0.1～40重量%である請求項1記載の電子写真用トナー。

【請求項3】 COOH基含有ビニル樹脂（B）中のCOOH基1当量当り、グリシジル基として0.01～0.5当量を有するグリシジル基含有ビニル樹脂（A）となる混合比率である請求項1記載の電子写真用トナー。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は電子写真、静電記録、静電印刷などに於ける、静電荷像を現像するための電子写真用トナーに関する。さらに詳しくは高速機に対応でき、しかも高解像度で且つ画質に優れた電子写真用トナーに関する。

【0002】

【従来の技術】 一般に、PPC複写機やプリンターに於ける電子写真用方法は、光感光体上に静電的潜像を形成し、ついで該潜像をトナーを用いて現像し、紙等の被定着シート上にトナー画像を転写した後、熱ロールで加熱圧着する方法が行われている。この方法は、加熱加圧下で定着を行うので迅速でしかも熱効率が極めて良好であり、従って定着効率が非常に良い。しかしながら、この熱ロール方式に於いては熱効率が良い反面、熱ロール表面とトナーが熔融状態で接触するため、トナーが熱ロール表面に付着転移し、次の被着シートにこれが再転移して汚す（オフセット現象）という問題がある。

【0003】 一方、複写機は、高速化の方向を指向しており、必然的に定着ロールのスピードも速くなり、短時間の加熱で定着出来るトナーが要求されている。出来るだけ短時間で定着させる為には熔融時高流動であることが必要で、そのためにはトナーに用いられる樹脂の分子量を小さくすれば良いと考えられているが、分子量低下による樹脂の凝集力が不足し、逆にオフセット現象が発生し易くなり、好ましくない。この為通常、流動性はある程度犠牲になるが、低分子量のものと高分子量のものと混合使用して、高分子量のものが有する凝集力と低分子量のものが有する流動性とでバランスを持たしている。このような例として、例えば、特公昭55-6895号公報、特公昭63-32180号公報、USP 4,921,771号等に係る

技術が提案されている。しかし、従来10～30枚/分のコピースピードの複写機が主流であったが、近年50～100枚/分の様な高速複写機も多数開発上市されている。このような高速化に対しては、いまだ充分ではなく、機械の改良等に対応している場合が多々ある。即ち、熱ロールの表面に布や紙でシリコンオイルを塗布してオフセットを防止している。この場合、機械の設備が複雑になるため、機械の補修、管理が複雑になり、コストアップに繋がり、好ましくない。したがって高速機用トナーで、且つシリコンオイル等のオイルの使用を必要としない定着用トナー（オイルレス定着方式）の開発が望まれている。又、プリンター性能のアップと共に原稿が非常に綺麗になり、原稿を出来るだけ忠実に再現出来るような複写機の出現も強く要求されるようになって来た。太い薄い線は太く薄く、細い濃い線は細く濃く、非常に細い線も全く同じ太さ同じ形に、原稿を出来るだけ忠実に再現することが必要で、この為には、非常に細かい線でも再現出来るようトナーの粒径も小さくする必要があり小粒径化トナーが要求されるようになってきた。しかし、折角小粒径化トナーを用いても、定着時熱ロールでトナーが潰されて大きく拡がってしまえば、細線が太くなり好ましくない。紙に定着した時のトナーの拡がり出来るだけ元のトナーの大きさを維持できるよう高解像度でしかも高画質のトナーが熱望されている。

【0004】 定着時熱ロールでトナーが潰されて大きく拡がらなくするためには、高分子量を出来るだけ多くしトナーに弾性を持たせればよいが、その場合粉碎し難く生産性がダウンし問題となる。また、高解像度でしかも高画質のトナーにするには一般に7 μ 位に小粒径化するのであるが、粉碎し易くするため、低分子量を増やすと粉碎時微粉が多量発生し、生産効率が落ち生産コストが大幅に上昇し問題となる。

【0005】 一方、オイルレス定着方式用トナーの開発に於けるオフセット防止方法としては架橋ポリマーを用いたトナーも数多く提案されている。例えば特公昭60-36582号公報等には、乳化重合法で製造された架橋ポリマーを用いる方法が開示されている。この場合、用いられる架橋ポリマーはゲル分を50～99%含有しており、このゲル分を多くすると、耐オフセット性は良くなるが粉碎性は悪化し、他方架橋ポリマー分が少なくなると粉碎性は良くなるが耐オフセット性は良ならず、耐オフセット性と粉碎性の両者を満足することは極めて困難であった。また、この方法では架橋ポリマー製造時に乳化粒子を安定化させるため分散剤や分散助剤を併用させる必要がある。これら分散剤は吸湿し易いため電気特性、特にチャージ安定性に悪影響を及ぼすので、架橋ポリマー製造後、できるだけこれらを取り除く必要がある。しかし、これらを洗浄して完全に取り除くには多大の労力が必要であり、また、洗浄水の排水量も多くなりその処理も大変である。また、USP4,966,829号公報には、ゲル

成分が0.1～60重量パーセント含み且つテトラヒドロフラシ可溶分に於いてメインピークの分子量が1,000～25,000、且つ、サブピーク又はショルダーの分子量が3,000～150,000が少なくとも一つ有するビニル系重合体を含有するトナーが良い旨開示されている。しかし、これを製造する方法はサスペンション法であり、この場合も乳化重合法と同じように、製造時に分散剤や分散助剤を併用させるので、上記乳化重合と全く同じ問題があった。この為、本発明者等は定着性の良いトナー用樹脂として、溶液重合法による樹脂(USP4,963,456号)を開発してきた。

【0006】溶液重合法による樹脂は、重合終了後溶剤を除去するが、この時、未反応の残存モノマーや開始剤の分解物等低揮発成分は全て留去出来るので、非常に不純物の少ない電氣的には安定な均質な樹脂が得られ、トナー用には最適のものが得られるものと考えられる。しかしながら、溶液重合法による架橋ポリマーの製造は、ワイゼンベルグ効果(攪拌棒に樹脂が巻きつく)が発生し製造出来なくなるという問題があった。したがって、本発明者等は、さらにバルク等で出来るだけ高分子化する方法(USP 5,084,368号)を開発した。しかし製造出来る高分子量のものには限界があり、オフセット性を完全に克服するところまでは至っていなかった。また、特公昭60-38700号公報には、グリシジル基含有単量体を3～40%有する共重合体(A)と架橋性化合物(B)とを加熱混合して製造したトナーバインダーが良い旨開示されているが、このトナーに於いてはエポキシ基が多量残っているため長期のテストで逆チャージのトナーが発生し耐久性に問題を生じていた。

【0007】

【発明が解決しようとする課題】本発明者らは、溶液重合法にて製造したCOOHを有する樹脂とグリシジル基を有する化合物を用いて特定の比率で架橋させることにより、高速機に対応でき、且つ定着性・オフセット性・ブロッキング性のバランスが良く、粉碎性、生産効率、電気特性、チャージ安定性にも優れたトナーを得る技術を開発(特開平06-011890号公報、特開平06-222612号公報)した。しかし、トナー製造工程における混練時に架橋成分に過剰なシェアーがかかりゲルが切断をうけるため、高温における弾性が不十分となり、定着後の画像の悪化や十分な耐オフセット効果が得られないという問題が生じた。本発明者らは、これらの要求を満足すべく鋭意検討した結果、グリシジル基を含有する架橋剤の分子量およびエポキシ価を改良することにより、トナー製造工程の混練時におけるゲルの切断が低減され、画像再現性、耐オフセット性に効果が表れ、定着性・オフセット性・ブロッキング性のバランスが大幅に改善され、且つ粉碎性、生産効率、電気特性、チャージ安定性にも優れたトナー用結着剤を見だし、本発明を完成した。

【0008】即ち、本発明は、1) 少なくとも着色剤

と結着剤からなる電子写真用トナーに於いて、当該結着剤が重量平均分子量が10,000より大きく100,000以下であり、エポキシ価0.005～0.1Eq/100gであるグリシジル基含有ビニル樹脂(A)を架橋剤とし、酸価1～30mg KOH/g、Tgが40～70℃であるCOOH基含有ビニル樹脂(B)よりなる樹脂組成物を主体として構成されていることを特徴とする電子写真用トナー、

2) 該結着剤が、グリシジル基含有ビニル樹脂(A)とCOOH基含有ビニル樹脂(B)とを加熱熔融することにより架橋反応せしめて得られたものの総量中に含まれるゲル分率が0.1～40重量%である請求項1記載の電子写真用トナー、

3) COOH基含有ビニル樹脂(B)中のCOOH基1当量当り、グリシジル基として0.01～0.5当量を有するグリシジル基含有ビニル樹脂(A)となる混合比率である請求項1記載の電子写真用トナーである。

【0009】

【課題を解決するための手段】本発明者らは、これらの要求を満足すべく鋭意検討した結果、グリシジル基を含有する架橋剤の分子量およびエポキシ価を改良することにより、トナー製造工程の混練時におけるゲルの切断が低減され、画像再現性、耐オフセット性に効果が表れ、定着性・オフセット性・ブロッキング性のバランスが大幅に改善され、且つ粉碎性、生産効率、電気特性、チャージ安定性にも優れたトナー用結着剤を見だし、本発明を完成した。

【0010】即ち、本発明は、1) 少なくとも着色剤と結着剤からなる電子写真用トナーに於いて、当該結着剤が重量平均分子量が10,000より大きく100,000以下であり、エポキシ価0.005～0.1Eq/100gであるグリシジル基含有ビニル樹脂(A)を架橋剤とし、酸価1～30mg KOH/g、Tgが40～70℃であるCOOH基含有ビニル樹脂(B)よりなる樹脂組成物を主体として構成されていることを特徴とする電子写真用トナー、

2) 該結着剤が、グリシジル基含有ビニル樹脂(A)とCOOH基含有ビニル樹脂(B)とを加熱熔融することにより架橋反応せしめて得られたものの総量中に含まれるゲル分率が0.1～40重量%である請求項1記載の電子写真用トナー、

3) COOH基含有ビニル樹脂(B)中のCOOH基1当量当り、グリシジル基として0.01～0.5当量を有するグリシジル基含有ビニル樹脂となる混合比率である請求項1記載の電子写真用トナーである。

【0011】

【発明の実施の形態】本発明に於けるグリシジル基含有ビニル樹脂(A)としては、重量平均分子量が10,000より大きく100,000以下、好ましくは12,000～30,000で且つエポキシ価が0.005～0.1Eq/100gであるものが好まし

い。グリシジル基含有ビニル樹脂とは、グリシジル基を含有するビニル単量体と他のビニル単量体を共重合して得られた樹脂である。重量平均分子量が10,000以下では、架橋体を合成してもトナー製造工程の混練におけるゲルの切断が激しく、定着後の画像再現性、耐オフセット性に問題が生じる。逆に100,000より高いと定着性が悪化する。また、エポキシ価は0.005~0.1Eq/100gの範囲のものが好ましい。0.005Eq/100g以下にあってはゲル生成量が少なくオフセット性の改良は出来ない。0.1Eq/100g以上では、架橋体を合成してもトナー製造工程におけるゲルの切断が激しく、画像再現性、耐オフセット性に問題が生じる。

【0012】本発明に於いてはグリシジル基含有ビニル樹脂(A)とCOOH基含有ビニル樹脂(B)を加熱溶解することにより架橋反応せしめた樹脂中に0.1~40%のゲル分率を含有していることが好ましい。さらに好ましくは5~20%である。ゲル分率0.1%以下では十分な架橋体が生成しておらず耐オフセット性の効果が発現しない。また40%以上では大部分がゲル化を起し流動性が悪化し定着性にも問題がでてくる。また、COOH基含有ビニル樹脂(B)中のCOOH基1当量当りグリシジル基として0.01~0.5当量を有するグリシジル基含有ビニル樹脂(A)となる混合比率が好ましい。さらに好ましくは0.03~0.2当量である。

【0013】本発明に於いて使用されるグリシジル基含有ビニル樹脂(A)の製造に用いられるグリシジル基含有ビニル単量体は、アクリル酸グリシジル、アクリル酸βメチルグリシジル、メタアクリル酸グリシジル、メタアクリル酸βメチルグリシジルなどが好ましい。

【0014】また本発明に於いて使用されるCOOH基含有ビニル樹脂(B)の製造に用いられるCOOH基含有ビニル単量体としては、アクリル酸、メタクリル酸、無水マレイン酸、マレイン酸、フマル酸、ケイヒ酸、フマル酸メチル、フマル酸エチル、フマル酸プロピル、フマル酸ブチル、フマル酸オクチル、マレイン酸メチル、マレイン酸エチル、マレイン酸プロピル、マレイン酸ブチル、マレイン酸オクチル等の不飽和二塩基酸のモノエステル類等である。

【0015】グリシジル基含有ビニル単量体及びCOOH基含有ビニル単量体と共重合するビニル単量体としては、例えば、スチレン、p-メチルスチレン、αメチルスチレン、ビニルトルエン等のスチレン類、アクリル酸メチル、アクリル酸エチル、アクリル酸プロピル、アクリル酸ブチル、アクリル酸オクチル、アクリル酸シクロヘキシル、アクリル酸ステアシル、アクリル酸ベンジル、アクリル酸フルフリル、アクリル酸ヒドロキシエチル、アクリル酸ヒドロキシブチル、アクリル酸ジメチルアミノメチル、アクリル酸ジメチルアミノエチル等のアクリル酸エステル類、メタアクリル酸メチル、メタアクリル酸エチル、メタアクリル酸プロピル、メタアクリル酸ブ

チル、メタアクリル酸オクチル、メタアクリル酸シクロヘキシル、メタアクリル酸ステアシル、メタアクリル酸ベンジル、メタアクリル酸フルフリル、メタアクリル酸ヒドロキシエチル、メタアクリル酸ヒドロキシブチル、メタアクリル酸ジメチルアミノメチル、メタアクリル酸ジメチルアミノエチル等のメタアクリル酸エステル類、フマル酸ジメチル、フマル酸ジブチル、フマル酸ジオクチル、マレイン酸ジメチル、マレイン酸ジブチル、マレイン酸ジオクチル等の不飽和二塩基酸のジエステル類、アクリロニトリル、メタアクリロニトリル、アクリルアミド、メタアクリルアミド、N置換アクリルアミド、N置換メタアクリルアミド、類のアミド等があり、これらのビニル単量体の少なくとも1種が用いられる。これらの中で特に好ましいビニル単量体としてはスチレン類、アクリル酸エステル類、メタアクリル酸エステル類、フマル酸ジアルキルエステル類、アクリロニトリル、アクリルアミド、メタクリルアミド等である。

【0016】COOH基含有ビニル樹脂(B)は、酸価1~30KOHmg/g、かつTgが40~70℃である樹脂が好ましい。さらに好ましくは酸価5~20KOHmg/g、Tgが50~60℃である。Tgが40℃以下ではブロッキングを起し好ましくなく、Tgが70℃以上になると軟化点が上昇し、定着性が悪化して本目的のトナーが得られない。COOH基含有ビニル樹脂(B)中のCOOH含有量は、酸価として1~30KOHmg/gが好ましい。1以下では一分子当たりの反応量が少なくなるため高分子量になり難く画像再現性、オフセット性が不足する。また30KOHmg/g以上では、トナー製造工程の混練におけるゲルの切断が激しく画像再現性、オフセット性が悪化する。

【0017】本発明における数平均分子量や重量平均分子量はGPC法により求めたもので、単分散標準ポリスチレンで検量線を作成した換算分子量である。測定条件は下記の通り。

GPC装置 ; JASCO TWINCLE HPLC
DETECTOR ; SHODEX RI SE-31
COLUMN ; SHODEX GPCA-80M*2+KF-802
溶 媒 ; TETRAHYDROFURAN
流 速 ; 1.2ml/min.

本発明におけるゲル分率は、樹脂5部を酢酸エチル95部に十分溶解させた時の樹脂全量に対する酢酸エチル不溶分を算出したものである。

【0018】

【実施例】次に実施例により本発明を具体的に説明する。なお、以降「部」は、特にことわらない限り重量部を表わす。

〔グリシジル基含有ビニル樹脂(A)の製造例〕

製造例A-1

キシレン75部を窒素置換したフラスコに仕込み昇温し、キシレン還流下において、予め混合溶解しておいたスチレン65部、アクリル酸n-ブチル30部、メタアクリル酸グ

リシジル5部、ジ-*t*-ブチルパーオキサイド1部を5時間かけて連続添加し、さらに1時間還流を継続する。その後内温 130℃に保ち、2時間の残モノマー重合を2回行うことにより反応を完結して、重合液を得た。これを160℃ 10mmHgのベッセル中にフラッシュして溶剤等を留去した。得られたビニル樹脂の重量平均分子量は40,000、エポキシ価0.035Eq/100gであった。

【0019】製造例A-2

製造例A-1においてジ-*t*-ブチルパーオキサイド1部を4部、メタアクリル酸グリシジル 5部を13部、スチレン65部を57部とした以外は製造例A-1と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

製造例A-3

製造例A-2においてジ-*t*-ブチルパーオキサイド4部を8部とした以外は製造例A-2と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

【0020】製造例A-4

製造例A-2においてメタアクリル酸グリシジル13部を16部、スチレン57部を54部とした以外は製造例A-2と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

製造例A-5

製造例A-1においてジ-*t*-ブチルパーオキサイド1部を4部、メタアクリル酸グリシジル5部を1部、スチレン65部を69部とした以外は製造例A-1と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

【0021】製造例A-6

製造例A-5においてジ-*t*-ブチルパーオキサイド4部を8部とした以外は製造例A-5と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

製造例A-7

製造例A-5においてメタアクリル酸グリシジル1部を0.5部、スチレン69部を69.5部とした以外は製造例A-5と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

【0022】製造例A-8

製造例A-1においてジ-*t*-ブチルパーオキサイド1部を0.4部、メタアクリル酸グリシジル5部を1部、スチレン65部を69部とした以外は製造例A-1と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

製造例A-9

製造例A-8においてジ-*t*-ブチルパーオキサイド0.4部を0.1部とした以外は製造例A-8と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

【0023】製造例A-10

製造例A-8においてメタアクリル酸グリシジル1部を0.5部、スチレン69部を69.5部とした以外は製造例A-8と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

製造例A-11

製造例A-1においてジ-*t*-ブチルパーオキサイド1部を0.4部、メタアクリル酸グリシジル5部を13部、スチレン65部を57部とした以外は製造例A-1と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

【0024】製造例A-12

製造例A-11においてジ-*t*-ブチルパーオキサイド0.4部を0.1部とした以外は製造例A-11と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

製造例A-13

製造例A-11においてメタアクリル酸グリシジル13部を16部、スチレン57部を54部とした以外は製造例A-11と全く同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

【0025】[COOH基含有ビニル樹脂(B)の製造例]

製造例B-1

スチレン57.4部、アクリル酸*n*-ブチル11.9部、メタアクリル酸0.7部とキシレン溶媒30部からなる溶液にスチレン100部当たり0.6部のジ-*t*-ブチルパーオキサイドを均一に溶解したものを、内温190℃内圧 6kg/cm²に保持した51の反応器に750cc/hrで連続的に供給して重合し低分子量重合液を得た。

【0026】別に、ビニル単量体として、スチレン75部、アクリル酸*n*-ブチル23.5部、メタアクリル酸1.5部を窒素置換したフラスコに仕込み、内温120℃に昇温後同温度に保ち、バルク重合を10時間行った。この時の重合率は51%であった。ついで、キシレン50部を加え、予め混合溶解しておいたジブチルパーオキサイドの0.1部キシレン 50部を130℃に保ちながら8時間かけて連続添加し、更に2時間残モノマー重合して、重合を完結し、高分子量重合液を得た。ついで、上記低分子量重合液100部と高分子量重合液60部とを混合した後、これを160℃10mmHgのベッセル中にフラッシュして溶剤等を留去した。得られたビニル樹脂のT_gは59℃、酸価は7.3であった。

【0027】製造例B-2

製造例B-1において低分子量重合液を製造する際に、スチレン57.4部を54.6部、メタアクリル酸0.7部を3.5部とした以外は全く製造例B-1と同様にしてビニル樹脂を得た。得られたものの物性値を表-2に示した。

製造例B-3

製造例B-1において低分子量重合液を製造する際に、

スチレン57.4部を53.2部、メタアクリル酸0.7部を4.9部とした以外は全く製造例B-2と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

【0028】製造例B-4

製造例B-1において低分子量重合液を製造する際に、スチレン57.4部を58.1部、メタアクリル酸0.7部を0.0部とし、また高分子量重合液を製造する際にスチレン75部を76.0部、メタアクリル酸1.5部を0.5部とした以外は全く製造例B-2と同様にしてビニル樹脂を得た。得られたものの物性値を表-1に示した。

製造例B-5

製造例B-4において高分子量重合液を製造する際に、スチレン75部を76.3部、メタアクリル酸1.5部を0.2部とした以外は全く製造例B-4と同様にしてビニル樹脂を得た。得られたものの物性値を表-2に示した。

【0029】製造例B-6

製造例B-1において低分子量重合液を製造する際に、スチレン57.4部を50.4部、アクリル酸n-ブチル11.9部を18.9部とした以外は全く製造例B-1と同様にしてビニル樹脂を得た。得られたものの物性値を表-2に示した。

製造例B-7

製造例B-1において低分子量重合液を製造する際に、スチレン57.4部を46.9部、アクリル酸n-ブチル11.9部を22.4部とした以外は全く製造例B-1と同様にしてビニル樹脂を得た。得られたものの物性値を表-2に示した。

【0030】製造例B-8

製造例B-1において低分子量重合液を製造する際に、スチレン57.4部を61.6部、アクリル酸n-ブチル11.9部を7.7部とした以外は全く製造例B-1と同様にしてビニル樹脂を得た。得られたものの物性値を表-2に示した。

製造例B-9

製造例B-1において低分子量重合液を製造する際に、スチレン57.4部を65.1部、アクリル酸n-ブチル11.9部を4.2部とした以外は全く製造例B-1と同様にしてビニル樹脂を得た。得られたものの物性値を表-2に示した。

【0031】実施例1

製造例A-1で得られたビニル樹脂3部、製造例B-1で得られたビニル樹脂97部をヘンシェルミキサーにて混合後、2軸混練機(KEXN S-40型、栗本鉄工所製)にて200℃で混練反応させた。冷却・粉碎後、カーボンブラックMA100(三菱化成製)8部、ポリプロピレンワックス(ビスコール550P)5部、荷電調整剤としてアイゼンスピロンブラックTRH1部添加し、再度ヘンシェルミキサーにて混合後、2軸混練機(PCM-30型、池貝鉄鋼製)にて150℃で混練させた。ついで冷却・粉碎・分級して約7ミクロンのトナーを得た。このトナー3部とキャリア97

部とを混合して現像剤とし、市販の高速複写機を改造して、画像を書かせて評価した結果を表-3に示す。

【0032】実施例2、3、4、5

実施例1において、製造例A-1で得られたビニル樹脂を製造例A-2、5、8、11で得られたビニル樹脂にした以外は実施例1と全く同様にし、各々実施例2、3、4、5とした。それらの結果を表-3に示す。

【0033】実施例6、7、8、9

実施例1において、製造例B-1で得られたビニル樹脂を製造例B-2、4、6、8にした以外は実施例1と全く同様にし、各々実施例6、7、8、9とした。それらの結果を表-3に示す。

【0034】実施例10

実施例6において、製造例A-1で得られたビニル樹脂と製造例B-1で得られたビニル樹脂の混合比率を97/3から94/6にした以外は実施例1と全く同様にした。その結果を表-3に示す。

【0035】比較例1、2、3、4、5、6、7、8

実施例1において、製造例A-1で得られたビニル樹脂を製造例A-3、4、6、7、9、10、12、13で得られたビニル樹脂にした以外は実施例1と全く同様にし、各々比較例1、2、3、4、5、6、7、8とした。それらの結果を表-4に示す。

【0036】比較例9、10、11、12

実施例1において、製造例B-1で得られたビニル樹脂を製造例B-3、5、7、9にした以外は実施例1と全く同様にし、各々比較例9、10、11、12とした。それらの結果を表-4に示す。

【0037】比較例13

実施例6において、製造例A-1で得られたビニル樹脂と製造例B-1で得られたビニル樹脂の混合比率を97/3から92/8にした以外は実施例1と全く同様にした。その結果を表-4に示す。

【0038】比較例14

実施例1において、製造例A-1で得られたビニル樹脂と製造例B-1で得られたビニル樹脂の混合比率を97/3から100/0にした以外は実施例1と全く同様にした。その結果を表-4に示す。

【0039】[トナーの評価方法]

1) 画像再現性

市販の高速複写機(72枚/分のコピースピード)で線幅約100μmの線を紙上に転写まで行い、マイクロスコープにて観察し線幅を5点測定した。さらにこの紙を定着機に通し、定着させた後の線幅5点を測定した。定着前後の線幅の平均をそれぞれ求め、定着前の線幅と定着後の線幅の差により以下のように評価した。

線幅増加分 δ = 定着後線幅 - 定着前線幅

◎ ; $\delta < 5\mu\text{m}$

○ ; $5 \leq \delta < 10\mu\text{m}$

× ; $\delta \geq 10\mu\text{m}$

【0040】2) 定着性

市販の高速複写機 (72枚/分のコピースピード) でコピーし、このコピーしたベタ黒部分と白地の間を消しゴム (トンボ鉛筆社製プラスチック消しゴム "MONO") により、一定の力で10回往復させ、ベタ黒部分の黒度をインキ濃度計で測定し、トナーの残存比率を濃度比で表し、80%以上を良好とした。

3) オフセット性

コピーした場合のオフセット発生する温度をそのまま表示し、200℃以上を良好とした。

【0041】4) ブロッキング性

トナーを温度50℃相対湿度50%の環境下に1週間放置した後の粉体の凝集の程度を目視にて以下のように測定した。

◎; 全く凝集していない

○; わずかに凝集しているが、容器を軽く振るとほぐれる

△; 容器をよく振ってもほぐれない凝集物がある

×; 完全に団塊化している

【0042】5) 粉碎性

トナー製造時、2軸混練冷却したものを一部採取して粉碎し、10メッシュアンダー16メッシュオンの粒度に揃えてジェットミルにて粉碎した。コールターカウンターにて粒度分布を測定、5~20μの粒度の割合を求める。

◎; 85%以上

○; 70~85%

△; 50~70%

×; 50%以下

【0043】

【表1】

製造例A

	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10	A-11	A-12	A-13
Mw	30000	11000	7000	11000	11000	7000	11000	70000	1E+05	70000	70000	1E+05	70000
酸価(Eq/100g)	0.035	0.009	0.009	0.11	0.007	0.007	0.004	0.007	0.007	0.004	0.09	0.09	0.11

【0044】

【表2】

製造例B

	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
酸価(mgKOH/g)	7.3	24.5	33.2	0.9	0.4	7.3	7.3	7.3	7.3
T _g (℃)	58	60	61	56	56	44	37	64	72

【0045】

【表3】

実施例

	実-1	実-2	実-3	実-4	実-5	実-6	実-7	実-8	実-9	実-10
樹脂A	A-1	A-2	A-5	A-8	A-11	A-1	A-1	A-1	A-1	A-1
樹脂B	B-1	B-1	B-1	B-1	B-1	B-2	B-4	B-6	B-8	B-1
重量比率(B/A)	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	94/6
ゲル分(%)	15	19	7	12	30	8	4	16	14	38
T _g (℃)	59	60	58	59	60	61	56	45	65	60
画像再現性b(μm)	◎ 3	○ 7	○ 7	○ 6	○ 8	○ 8	○ 9	○ 5	○ 5	◎ 2
定着性(%)	◎ 92	○ 86	◎ 93	◎ 92	△ 82	◎ 90	◎ 94	◎ 97	○ 86	△ 81
オフセット性(℃)	◎ 230	△ 205	△ 210	○ 225	△ 210	△ 210	△ 205	○ 225	◎ 230	◎ 240
保存性	○	○	○	○	○	◎	○	△	◎	○
粉碎性(%)	◎ 90	◎ 89	◎ 90	◎ 90	◎ 88	◎ 90	◎ 91	◎ 89	◎ 90	◎ 88

【0046】

【表4】

比較例

	比-1	比-2	比-3	比-4	比-5	比-6	比-7	比-8	比-9	比-10	比-11	比-12	比-13	比-14
樹脂A	A-3	A-4	A-6	A-7	A-9	A-10	A-12	A-13	A-1	A-1	A-1	A-1	A-1	A-1
樹脂B	B-1	B-1	B-1	B-1	B-1	B-1	B-1	B-1	B-3	B-5	B-7	B-9	B-1	B-1
重量比率(B/A)	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	97/3	92/8	100/0
ゲル分(%)	11	28	5	4	30	3	36	38	2	1	15	14	45	0
T _g (℃)	59	60	58	58	59	58	61	61	58	58	38	72	62	58
画像再現性 δ (μ m)	○ 9	○ 9	○ 9	× 11	◎ 2	× 10	○ 8	× 10	× 11	× 13	○	◎	◎	×
定着性(%)	◎ 91	△ 82	◎ 93	◎ 94	× 79	○ 89	× 78	× 79	◎ 93	◎ 94	◎ 98	× 76	× 75	◎ 94
オフセット性(℃)	× 195	× 190	× 195	× 195	◎ 240	× 195	△ 210	△ 200	× 195	× 185	○ 220	◎ 235	◎ 240	× 180
保存性	○	○	○	○	○	○	◎	◎	○	○	×	○	○	○
粉碎性(%)	◎ 90	◎ 88	◎ 91	◎ 90	◎ 88	◎ 90	◎ 87	◎ 88	◎ 90	◎ 91	◎ 90	◎ 90	◎ 87	◎ 90

【0047】

【発明の効果】表-3に示した如く、本発明の方法により製造されたトナーは画像再現性、耐オフセット性に優

れ、また定着ブロッキング性のバランスも良く、粉碎性も良好で実用上優れた性能を有している。